OPTICAL AND STRUCTURAL PROPERTIES OF AMORPHOUS CARBON THIN FILMS DEPOSITED BY MICROWAVE SURFACE-WAVE PLASMA CVD

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Abstract

Nitrogen doped amorphous carbon (a-C:N) thin films were deposited on silicon and quartz substrates by microwave surface-wave plasma chemical vapor deposition technique at low temperature (< 100 ^{o}C). We used argon (Ar), camphor dissolved in alcohol and nitrogen (N) as carrier, source and dopant gases respectively. Optical band gap decreased from 4.1 eV to 2.4 eV when N_2 gas concentration increased from 0% to 4.5%. The films were annealed at different temperatures ranging from 150 to 450 ^{o}C in Ar gas environment for 30 min to investigate the optical properties of the films before and after annealing. The optical band gap remained constant (2.4 eV) until 150 ^{o}C annealing and beyond that it decreased dramatically to 1.1 eV at 400 ^{o}C annealing. The structural modification of the films leading to graphitization as a function of the annealing temperature was confirmed by the characterization of Raman spectra.

Introduction

The cost reduction of solar cell and establishment of environmentally friendly production process are very important for further spread of photovoltaic technology. Carbon (C) is a material of highly stable, cheap and non-toxic, which can be obtained from precursors those, are sufficiently available in nature. Furthermore, amorphous carbon (a-C) has been an attractive material for the fabrication of photovoltaic solar cells because of its outstanding properties such as chemical inertness, high hardness, high electrical resistivity, high thermal conductivity, high dielectric strength, infrared optical transparency and optical band gap varying over a wide range from about 5.5 eV for insulating diamond to 0.0 eV for metallic graphite [1]. Impurity doping, such as nitrogen (N), phosphorus (P) and Iodine (I) can modify optoelectronic properties of the films by increasing either the electron or hole concentration in the semiconductor device. In addition, structural properties of the films can be changed due to the effect of annealing; the ratio of hybridized bonds like trigonal (sp^2) and tetragonal (sp^3) in carbon film can be tuned by appropriate annealing temperature. In this paper, we report the optical and structural properties of N doped a-C (a-C:N) thin films deposited on silicon (Si) and quartz substrates by microwave (MW) surface-wave plasma (SWP) chemical vapor deposition (CVD), a newly developed C thin film deposition method, before and after annealing the films. Our experimental purpose is to control properties of the films suitable for solar cell application.

Results and discussion

To study the optical characteristics of both the as-deposited and the annealed films, we carried out the reflectance and transmittance measurements by UV/VIS/NIR spectrophotometer in the range of 200-2000 nm. The absorption coefficient (α) was calculated by the spectral reflectance and transmittance, and the film thickness data. The film thickness was measured by Nanopics 2100/NPX200 surface profiler. The optical band gaps were obtained by Tauc plot. The Tauc optical band gap (Eg) was obtained from the extrapolation of the linear part of the curve at α = 0 by using the Tauc equation,

$$(\alpha h\nu)^{1/2} = B(Eg - h\nu) \qquad (1)$$

where B is the density of the localized state constant [2].

Fig. 1 shows that optical band gap decreased almost exponentially with increasing N_2 concentration during film deposition. The minimum optical gap is found 2.4 eV when N_2 concentration is 4.5 %. This result suggests that the doping of N_2 during film deposition can reduce the optical band gap to some extent. Chen and Robertson have also reported the qualitatively similar effect of N_2 doping on optical band gap[3]. XPS measurement gave information of chemical composition in the as-deposited film; the peak position of carbon (C) 1s, nitrogen (N) 1s and oxygen (O) 1s are at 281.1 eV, 396 eV and 529.7 eV respectively. The optical band gap (2.4 eV) of our a-C:N film is still high for solar cell application. Previous researches showed that annealing of a-C films could reduce the band gap of the films[4]. In order to examine the annealing effects in our films, the films were annealed at different temperatures (0 to 450 ^oC). Fig. 1 shows a plot of optical band gap versus annealing temperature. The optical band gap (2.4 eV) remained constant as of as-deposited film until 150 ^oC annealing, and beyond that it decreased monotonically to 1.1 eV at 400 ^oC. Upon annealing, the films would turn to be more graphite like in nature as sp^2 bonds start to dominate sp^3 bonds in the carbon films. Fig. 2 shows Raman spectra of the as-deposited and the annealed a-C:N films. It is clear that the broad band of the as-deposited film gradually splitted into two peaks (commonly known as D and G lines) with increasing annealing temperature. Moreover, the slight up shift of G line towards higher wave number (above 1580 cm^{-1}) indicates that the films progressively changed to graphite in nature and crystalline have a very small grain size with increasing annealing temperature [5].Our results show that it is possible to control optical band gap of a-C thin films partially by N doping during film deposition and largely by post growth annealing of the films.

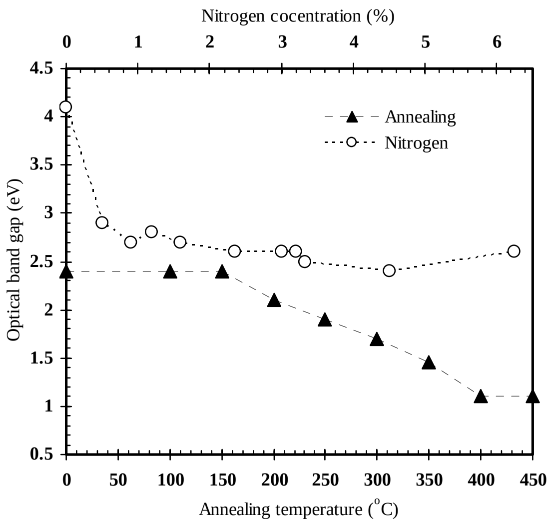

Figure* 1. *Optical band gap versus Annealing temperature and Nitrogen concentration.

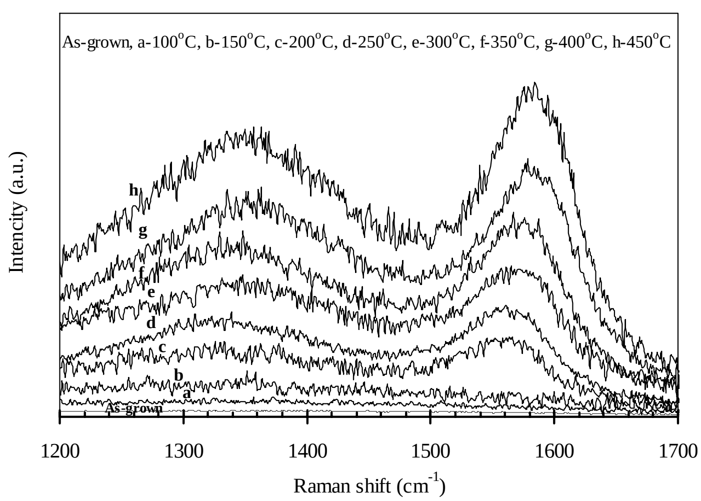

***Figure* 2. *Raman spectra of the as-deposited and the annealed a-C:N films at various temperatures*.**

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